The Molecular Formula of Cephalosporin P_1

By T. G. HALSALL, E. R. H. JONES, and G. LOWE
(THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY)

THE chemistry of the steroidal antibiotic cephalosporin P_1 has so far been discussed[1] in terms of a molecular formula $C_{32}H_{48}O_8$ and a parent skeleton of 28 carbon atoms, the molecular weight having been determined by the *X*-ray crystallographic method. Recently a C_{29} carbon skeleton has been proposed[2] for fusidic acid, a similar steroidal antibiotic. The molecular formula of cephalosporin P_1 has now been found to be $C_{33}H_{50}O_8$, the molecular weight having been kindly determined for us in the laboratory of Professor C. Djerassi at Stamford University by mass-spectrometric examination of cephalosporin P_1 methyl ester and dideacetylcephalosporin P_1 lactone, using an improved injection technique. The parent skeleton has therefore 29 carbon atoms and an additional methyl group is presumably present, probably at position 8 of the basic steroid ring system. The implications of this closer relationship of cephalosporin P_1 to fusidic acid are being examined.

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A Kinetic Measurement for Fast Cation–Cation Oxidations in Solution

By M. J. NICOL
(UNIVERSITY OF THE WITWATERSRAND, SOUTH AFRICA)
and D. R. ROSSEINSKY
(UNIVERSITY OF EXETER)

THE use of rotating platinum electrodes in polarography, hitherto confined to oxidations involving only one ionic reactant,[1] can be extended to kinetic investigation of fast calomel–cation oxidations provided there exists a suitable applied voltage at which only one species gives a diffusion current. Thus if such an electrode in the system $Fe^{II} + V^{V} \xrightarrow{k_1} Fe^{III} + V^{IV}$ (in M-perchlorate), is connected by perchlorate solution as a bridge to a standard calomel electrode, and if a potential of 1·0v is applied across the cell, then a diffusion current i_d passes that is proportional only to the iron(II) concentration. Tests for electrode catalysis were negative. From second-order plots based on pen-recorder traces of the diffusion current against time, the rate constant k_1 showed an approximately 1·08th-power dependence on the (excess) hydrogen-ion concentration, indicating the following mechanism:

$$H^+ + VO_2^+ + Fe^{2+} \xrightarrow{k_2} HOVO^+ + Fe^{3+}$$

$$H^+ + HOVO^+ \longrightarrow H_2OVO^{2+} \text{ (rapid)}$$

(Protonation of VO_2^+ may actually occur in a pre-equilibrium; the non-integral 1·08th order arises from marginal participation of diprotonated VO_2^+ or from an inconstancy of activity coefficients with medium changes[2]). The rate constant k_2 is $1{\cdot}15 \times 10^5$ l. mole^{-1} sec.$^{-1}$ at 0°, E_a being 3·60 kcal./mole and $\Delta S_{25}{}^* -33$ e.u. These values are consistent with the view that predominantly electrostatic effects accompanying the accumulation of charge.

Further reactions apparently amenable to this technique are the interactions Mn^{III}–V^{IV}, Mn^{III}–Fe^{II}, and Co^{III}–Fe^{II}.[3] The rate constant of the last reaction does not conform with the Marcus equation,[4] $k_{ox} = (k'k''K)^{\frac{1}{2}}$, k_{ox} (calc.)[5] being 5×10^9, and k_{ox} (obs.)[3] being 23 l. mole^{-1} sec.$^{-1}$. Conformance is expected because of close simulation by such transition-ion oxidations of the corresponding electron-exchange reactions (k' and k''), but it requires also a low equilibrium constant K. More favourable test reactions are V^{III}–Cr^{II} and Co^{III}–Mn^{II}, where k_{ox} (calc.)[5] are 3×10^{-2} and 3×10^3 l. mole^{-1} sec.$^{-1}$. respectively.

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